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PB-290 105

Utilization of Lime/Limestone Waste in a New Alumina Extraction Process

TRW, Inc, Redondo Beach, CA

Prepared for

Industrial Environmental Research Lab, Research Triangle Park, NC

Nov 78

PB 290105

United States
Environmental Protection
Agency

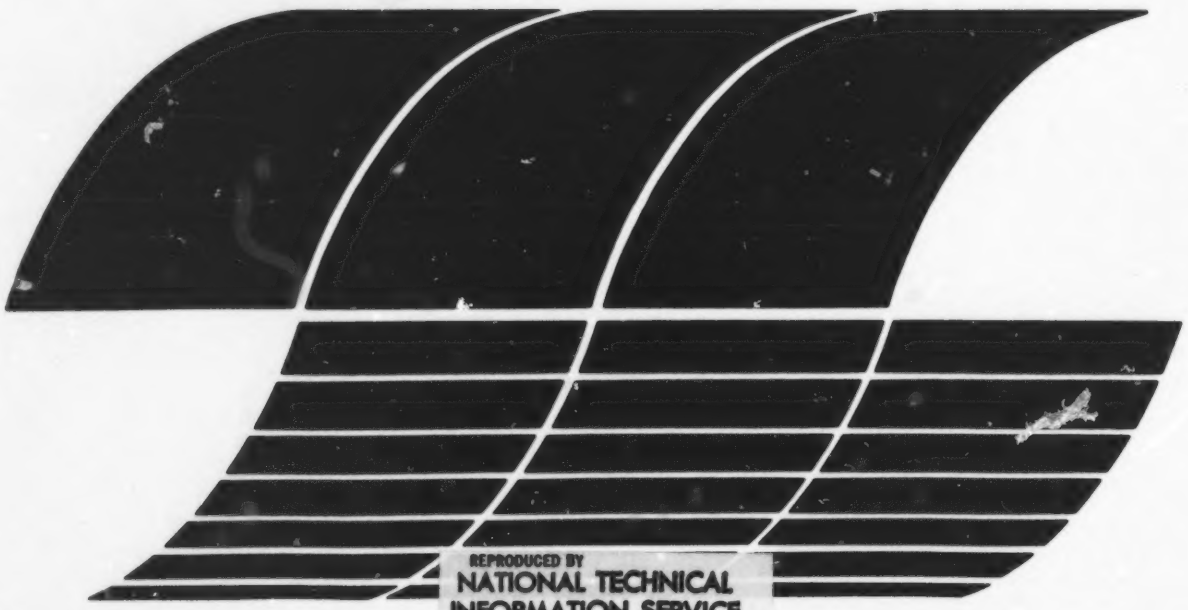
Industrial Environmental Research
Laboratory
Research Triangle Park NC 27711

EPA-600/7-78-225
November 1978

EPA

Utilization of Lime/Limestone Waste in a New Alumina Extraction Process

Interagency Energy/Environment R&D Program Report



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TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-600/7-78-225		PB290105

4. TITLE AND SUBTITLE	5. REPORT DATE
Utilization of Lime/Limestone Waste in a New Alumina Extraction Process	November 1978
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
E. P. Motley and T. H. Cosgrove	
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
TRW, Inc. One Space Park Redondo Beach, California 90278	EHE624A
	11. CONTRACT/GRANT NO.
	68-02-2613, Task 14
12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
EPA, Office of Research and Development Industrial Environmental Research Laboratory Research Triangle Park, NC 27711	Task Final; 4-9/78
	14. SPONSORING AGENCY CODE
	EPA/600/13

15. SUPPLEMENTARY NOTES IERL-RTP project officer is Julian W. Jones, MD-61, 919/541-2489.

16. ABSTRACT The report gives results of a preliminary process design and economic evaluation of a process for using lime/limestone scrubbing wastes as a source of calcium in the extraction of alumina (for use in aluminum production) from low grade domestic ores such as clays and coal ash. The other principal process feedstocks are soda ash and coal. The products are alumina, elemental sulfur, and dicalcium silicate, an alternate feedstock in the manufacture of portland cement. The conceptual plant is located next to a 1000 MW coal-burning power plant which generates > 1 million tons per year (tpy) of lime/limestone scrubber wastes. The required selling price for the alumina produced at 10% discounted cash flow would be $195-370 per ton, depending on the credit for sludge removal, exclusive of cement manufacture. If the alumina plant were co-located with an 860,000 tpy portland cement plant selling cement at $50 per ton, the required alumina selling price would be $27-221 per ton. Based on the current market price for alumina ($160 per ton), the portland cement plant appears to be necessary to make the process viable. In addition to the scrubber wastes, the process requires 12,000 tpy of soda ash, 300,000 tpy of clay, and 273,000 tpy of coal to produce 70,000 tpy of alumina, 156,000 tpy of sulfur, and 625,000 tpy of dicalcium silicate (used to produce 860,000 tpy of portland cement).

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
Pollution	Scrubbers	Pollution Control	13B	13I
Aluminum Oxide	Calcium	Stationary Sources	07B	
Extraction	Aluminum Industry	Alumina Extraction	13H,07A	11F
Waste Treatment	Clays	Scrubbing Waste		08G
Calcium Oxides	Sodium Carbonates	Coal Ash		
Calcium Carbonates	Coal	Dicalcium Silicate		21D
Sulfur	Portland Cements			11B

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS (This Report)	21. NO. OF PAGES
Unlimited	Unclassified	59
	20. SECURITY CLASS (This page)	22. PRICE
	Unclassified	PC A04/MF A01

EPA Form 2220-1 (9-73)

EPA-600/7-78-225

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by

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TRW, Inc.
One Space Park
Redondo Beach, California 90278

Contract No. 68-02-2613
Task No. 14
Program Element No. EHE624A

EPA Project Officer: Julian W. Jones

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Research Triangle Park, NC 27711

Prepared for

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Research and Development
Washington, DC 20460

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FOREWORD

Man and his environment must be protected from the adverse effects of pesticides, radiation, noise, and other forms of pollution, and the unwise management of solid waste. Efforts to protect the environment require a focus that recognizes the interplay between the components of our physical environment--air, water, and land. The Industrial Environmental Research Laboratory contributes to this multidisciplinary focus through programs engaged in

- studies on the effects of environmental contaminants on the biosphere, and
- a search for ways to prevent contamination and to recycle valuable resources.

This report, prepared by TRW Systems for the Environmental Protection Agency, Industrial Research Laboratory, Research Triangle Park, North Carolina, presents the results of a four month study to evaluate a new alumina extraction process which utilizes as a feedstock lime/limestone waste generated in the removal of sulfur dioxide (SO_2) from stack gases of coal burning power plants. This study includes a base case preliminary process design and economic evaluation, an applicability evaluation and an investigation of the critical/cost sensitive areas of the process.

ABSTRACT

This report describes results of a preliminary process design and economic evaluation of a processing scheme for using lime/limestone scrubbing wastes as a source of calcium in the extraction of alumina (for use in aluminum production) from low grade domestic ores such as clays or coal ash. The other principal feedstocks for the process are soda ash and coal. The products are alumina, elemental sulfur and dicalcium silicate, an alternate feedstock in the manufacturing of portland cement.

The conceptual plant is located next to a 1000 MW coal burning power plant which generates more than 1,000,000 tons per year (TPY) of lime/limestone scrubber wastes. In addition to the scrubber wastes, the process will require, yearly, 12,000 tons of soda ash, 300,000 tons of clay and 273,000 tons of coal to produce 70,000 tons of alumina, 156,000 tons of sulfur and 625,000 tons of dicalcium silicate. Dicalcium silicate can be used to produce 860,000 tons of portland cement per year. The required selling price for the alumina produced at 10 percent discounted cast flow (DCF) would range from $195 to $370 per ton as a function of sludge removal credit, exclusive of cement manufacture. However, if this alumina plant were co-located with a 860,000 TPY portland cement plant selling cement at $50 per ton, the alumina produced would have a range of selling prices, depending on sludge removal credit, of from $27 to $221 per ton at 10 percent DCF.

The chemistry of the process is similar to that for the lime-soda-sinter reaction except that the reaction proceeds in a reducing rather than an oxidizing atmosphere. The reaction is summarized as follows:

Sludge + Soda + Clay → Soluble Sodium Aluminate + Insoluble Dicalcium Silicate or, $4CaSO_4 + Na_2CO_3 + Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ + Reducing Combustion Gases → $Na_2O \cdot Al_2O_3 + 2SiO_2 \cdot (2CaO) + H_2S$ + Combustion Gases.

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SECTION 1
INTRODUCTION

The first generation of flue gas desulfurization systems is presently expanding in usage throughout the electrical power industry. These systems consist primarily of lime or limestone stack gas scrubbers in which the alkaline earths react with flue gas sulfur dioxide to form calcium sulfates and sulfites. The reactions transpire in a water slurry (wet scrubber) and produce large quantities of waste material identified as sludge. The solid portion of the sludge consists of calcium-sulfur compounds, fly ash, and calcium carbonate. The liquid portion of the sludge contains calcium, chloride and sulfate ions, and may contain sodium and magnesium ions along with ions of trace elements primarily from the fly ash. Because of this composition, there is concern the contamination of natural water supplies may occur through percolation to ground or surface waters in the vicinity of sludge disposal sites. Thus, alternate methods of treating and/or disposing of scrubber waste sludge are being studied.

The study presented herein investigates the commercial utilization of calcium sulfate/sulfite sludge as a coreactant in the extraction of alumina from an aluminosilicate ore, kaolin clay. The study provides a preliminary process design and economic evaluation of a hypothetical plant situated in the southeastern United States which utilizes the sludge output from a 1000 MW power plant stack gas scrubber. Although alumina is the desired product of the process, dicalcium silicate, and alternate feedstock in cement manufacture*, is also produced in large quantities in addition to high purity sulfur. As a result, a process complex which includes a proportionately sized cement plant has been assessed as the most economically viable arrangement. The industrial complex is co-located with the electrical power plant.

*Tricalcium silicate is normally used.

Present alumina production in the United States is based exclusively upon the Bayer process, or variations thereof, which utilize bauxitic ore feedstocks. Domestic production of bauxite is approximately 10 percent of consumption with dependence for the remaining supply centered on the Caribbean area and other sources external to the United States. Domestic reserves have been estimated (1965) at 45 MM tons* or 0.8 percent of the total world supply. The annual U.S. demand for aluminum metal is expected to be at least 21.2 MM tons of bauxite by the year 2000. This latter figure is roughly equivalent to 41.4 MM tons of bauxite ore. The insufficiency of U.S. domestic bauxite reserves is therefore obvious and a need exists to investigate alternate mineral sources of aluminum and related processes for the extraction of same. This fact is compounded by the equally obvious susceptibility to increase that imported bauxitic ore prices may have in future international markets.

Alternate sources of aluminum exist in abundance within the continental United States. These sources take the form of large low-grade bauxitic clay deposits, thin or deeply buried bauxite deposits, low-grade gibbitic bauxite, low-grade ferruginous bauxite, nonbauxitic clays of the kaolin type, anorthosite, dawsonite and alunite. The ultimate source of aluminum is expected to include a nonbauxitic clay of the kaolin type.

*Metric conversions are provided in Appendix A.

SECTION 2

CONCLUSIONS

The results of this study indicate that an alumina extraction process employing calcium sulfate/sulfite sludge, sodium carbonate and kaolin clay as coreactants could be commercially feasible* under present economic conditions provided that the alumina extraction plant includes a cement producing facility which utilizes the dicalcium silicate by-product from the alumina extraction process as feedstock. Should bauxite prices escalate, the estimated selling price for alumina as output from an alumina plant not possessing a cement facility may become competitive. Each of the above conclusions are based upon a sulfur credit of $10 per ton and a sludge disposal credit of $5 per wet ton (50 percent solids). These credits are considered conservative. The process is illustrated in Figure 1. The 10 percent discounted cash flow (DCF) price for alumina from a lime/limestone sludge utilization facility is $124 per ton including a sludge disposal credit and sulfur and cement by-product credits. Without these credits, the price of alumina from this process is $421 per ton. The current market value of alumina (from bauxite) is $160 per ton.

Up to 1.4 million tons of sludge per year may be produced by one 1000 MW generating facility. In the conceived process, this output is effectively converted into alumina, cement and sulfur. Yearly output from the complex is approximately 858,000 tons of cement, 70,000 tons of alumina and 156,000 tons of sulfur. The required alumina selling price for the base case alumina plant, exclusive of cement manufacture, is $292 per ton at a 10 percent DCF rate of return. When total utilization of the alumina plant by-products is considered,

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* Under the assumption that the chemistry will proceed at satisfactory rates with a minimum of side reactions. This assumption must be verified at bench and pilot scale levels.

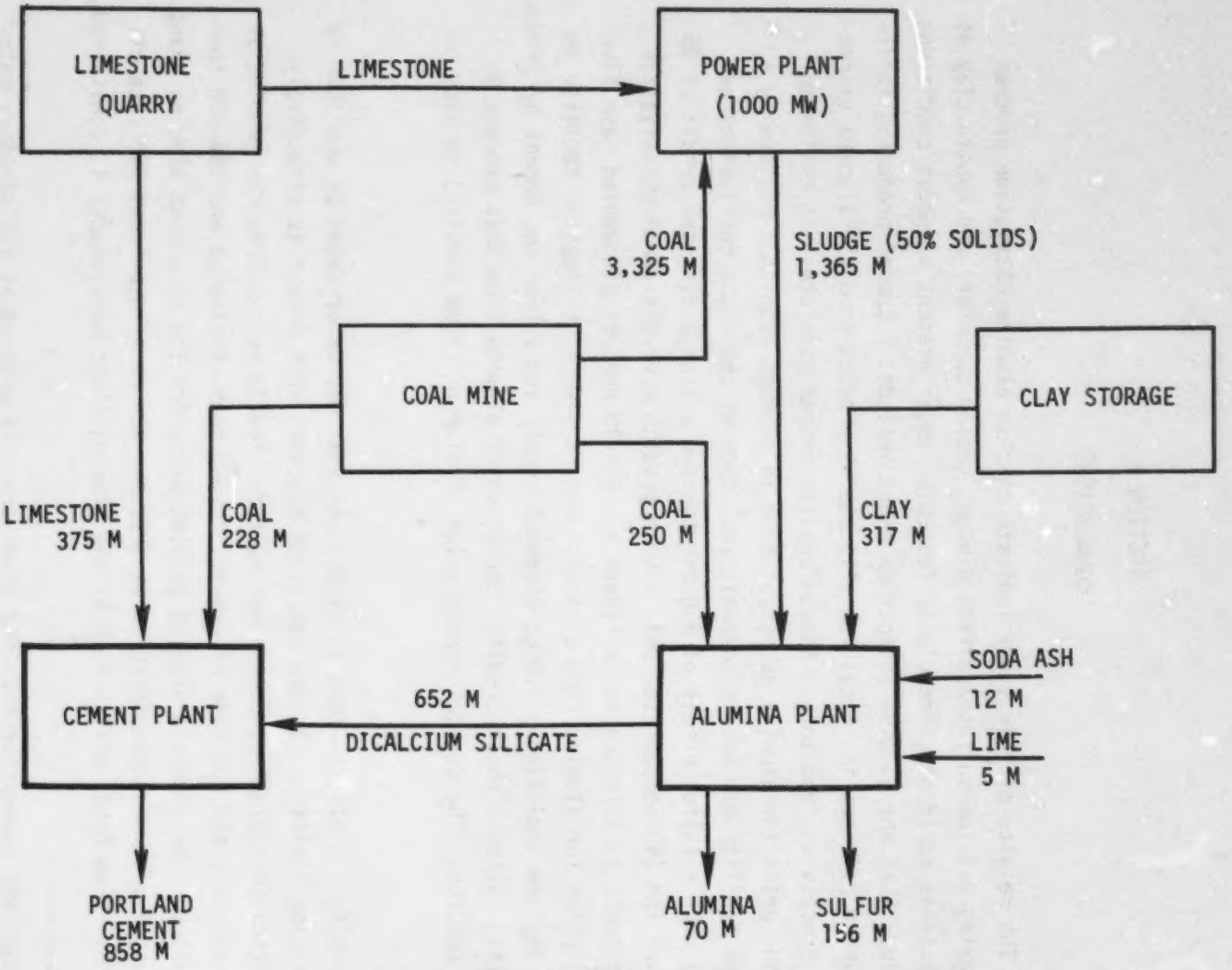

Figure 1. Total Utilization Concept
(Quantities in tons/yr)

i.e., cement manufacture with cement sold at $50 per ton, the selling price of alumina drops to $124 per ton at a 10 percent DCF rate of return and $182 per ton at a 12 percent DCF rate of return. These latter prices compare favorably with the present market value of alumina as produced from bauxite of $160 per ton. In each of the above cases, a sulfur credit of $10 per ton and a sludge disposal credit of $5 per wet ton (50 percent solids) were assumed.

Alternate means of sludge disposal are available to power utilities. Depending on the disposal site and applicable regulations, these include ponding and landfill of both treated and untreated waste. Present cost for chemical treatment range from $7.50 to $11.40 per wet ton (50 percent solids)[1]. Estimates for ponding run slightly lower but do not include disposal site and reclamation subsequent to pond life. Based on these cost estimates, sludge credits of $5 to $10 per wet ton are felt to represent complete disposal/utilization of the waste material, and therefore are used in this study.

The chemical functioning of this process is predicted upon several technical assumptions (see Recommendations, Section 3). The validity of these assumptions must be proven via laboratory experimentation before it may be concluded that the potential for a technically viable extraction process exists. Other elements of the process not dependent upon the referenced assumptions have been demonstrated in earlier work by the Bureau of Mines[2,3] and TRW Systems Inc.[4]. Given the laboratory demonstration of the validity of the process chemistry assumptions, sufficient technical justification will exist to proceed with a development program. No unusual equipment has been identified and plant construction can be accomplished with standard items.

SECTION 3

RECOMMENDATIONS

Technical assumptions are implicit in the conceived design. Laboratory verification of these assumptions is necessary before any developmental work may proceed. It is recommended that laboratory investigation be conducted to verify that:

- the reactions of soda, alumina, calcium and silica to form dicalcium silicate and sodium aluminate will proceed in a reducing atmosphere to a high percentage completion;
- the reaction rates are sufficiently fast to be practical;
- side reactions do not occur which inhibit the formation of soluble sodium aluminate and thus negate the output of alumina;
- coal can be used to produce a reducing atmosphere in the proper amounts in this processing scheme;
- the dicalcium silicate by-product possesses the necessary mechanical properties for compatibility with standard cement manufacture.

It is additionally recommended that an alternate processing scheme in which the principal product is cement (tricalcium silicate), be considered. This latter scheme would use sand and lime/limestone scrubber sludge as primary feedstocks. Physically, the design of such a process need not extend beyond grinding of the kiln sinter and hence would require significantly less capital than the alumina extraction process. Such a process would also be less energy intensive. Because of the potential for increased economic leverage implied in this scheme, a preliminary study for the purpose of assessing technical viability and quantifying the economic variables is recommended.

SECTION 4

TECHNICAL DISCUSSION

CHARACTERIZATION OF SCRUBBER WASTE

Table 1 presents reported data on sludge composition derived from a number of flue gas desulfurization (FGD) demonstration scrubbers based on limestone, lime, and double-alkali scrubbing. As indicated in Table 1, the sludges were generated from the scrubbing of flue gas (FG) originating from the combustion of fuels of substantially different sulfur and ash content (columns 2 and 3), scrubbed under a variety of conditions (columns 5, 6, and 7), and with or without simultaneous ash removal (column 8). The scrubbing system can be either closed or open loop (column 4). A closed loop system is one in which the only liquid that leaves the system is that occluded with the solids. Conversely, an open loop system has a direct liquid discharge. Thus, the sludge compositions presented represent a good sample of the spectrum of waste sludges expected from FGD throwaway processes.

The common components in all FGD waste sludges are calcium sulfite, calcium sulfate, calcium carbonate, and water. Limestone scrubber sludges contain substantial quantities of unreacted limestone. Double-alkali sludges contain minor quantities of alkali metal sulfites and sulfates. All these sludge components influence, at least to a minor extent, the cost of producing alumina from clays. Ash may or may not have an influence on the cost of the process depending on its composition.

Alumina production from clays requires calcium and alkali metal oxides as process feeds in addition to clay. The large concentration of calcium in flue gas desulfurization waste sludges renders them an attractive feedstock for the alumina process. The oxidation state of the sulfur is expected to have little influence on the alumina production process except as it affects the water content of the slurry. Sulfite is preferable to sulfate because of higher

TABLE 1. FDS SCRUBBER SLUDGE CHARACTERISTICS

Facility	Coal Sulfur	Coal Ash	Type	Scrubber Stoichiometery Ca/SO_2 (mole/mole)	Scrubber pH in Scrubber	O_2/SO_2 (mole/ratio)	Fly Ash* (%)	Sludge Composition (Dry Basis, Wt. %) $CaSO_3$ $1/2\ H_2O$ (%)	$CaSO_4$ $2H_2O$ (%)	$CaCO_3$, or CaO (%)	Na_2SO_4	Solids Content in Sludge (Wt %)
Kansas City Power & Light Hawthorne 4	3	13	Limestone Closed Loop	1.5	5.5-4.5	20	45	17	23	15	~0	40
Commonwealth Edison, Will County 1	3.5	15	Limestone Open Loop	1.5	5.9-5.7	40	15	50	15	20	~0	35
City of Key West Stock Island	2.0 (oil)	.04	Limestone Open Loop	5.0	7.5-6.5	30	1	20	5	74	~0	50
Kansas City Power & Light, LaCygne	5.3	22	Limestone Closed Loop	1.9	6.0-5.6	30	15	40	15	30	~0	35
Arizona Public Service Cholla	.5	10	Limestone Open Loop	1.0	6.5-5.2	100	65	15	20	0	~0	50
Shawnee	3.5	12	Limestone Closed Loop	1.2	7-6	30	37.9 34.7 38.3	30.4 33.1 30.9	14.5 17.2 16.6	21.8 19.7 11.9	~0 ~0 ~0	36.5 37.2 33.3
Shawnee	3.5	12	Lime Closed Loop	1.0	9-5	30	42.5 46.9	46.5 38.6	11.8 14.1	3.4 3.9	~0 ~0	46 46
Louisville Gas & Electric Paddy's Run	3.7	14	Lime Closed Loop	1.0	9.0-5.3	30	4	94	2	0	~0	40
So. Cal. Edison Mohave 2	.4	16	Lime Closed Loop	1.0	9-5	300	3	2	95	0	~0	65
FMC Mobile Scrubber	4.8	NA	Double Alkali	1.05	6-7	23	21.4	73.5		1.75	1.18	65
GM Parma, Ohio Chevrolet Plant	2.5	NA	Double Alkali	1.5	9 in 5.5-6 out	1000	1-2	85-73 ($CaSO_x$)		10-20 ($Ca[OH]_2$)	4-5	50
Kawasaki/Kureha	1.2-1.5 (oil)	NA	Double Alkali	1.0	6.9-7.3	37	Low	~100		<300 ppm		40
Showa Denka KK/Ebara	2.5-3.0 (oil)	NA	Double Alkali	NA	6.3	NA	Low	~100		<300 ppm		NA
Envirotech	.4	NA	Double Alkali	1.1-1.5	7.5-7.7 in 6.5 out	33	1-2	87-81 ($CaSO_x$)		10-15	2	60-70
Selected Base Case for Alumina Process	3.5	12	Lime	1.0	9-5	30	2	70	23	5	~0	46

* Typical ash composition: Silica (SiO_2)=47, Alumina (Al_2O_3)=25, Ferric Oxide (Fe_2O_3)=20, Lime (CaO)=3, Potassium Oxide (K_2O)=1.5, Magnesia (MgO)=.5, Sodium Oxide (Na_2O)=.5, Titanium Dioxide (TiO_2)=1, Sulfur Trioxide (SO_3)=1, Carbon (c)=2, Phos Pentoxide (P_2O_5)=.1.

calcium content per unit weight. However, dewatering the sulfite requires more energy than dewatering the sulfate. Water may have a beneficial effect in the blending of the process feedstock but it will affect adversely process energetics. Everything else being equal, the presence of alkali metals in the sludge is highly desirable. Ash may be considered as clay; therefore, its desirability as a sludge component depends on its alumina concentration. Although the composition of coal ash is extremely variable, the Al_2O_3/SiO_2 ratio for a typical coal ash is 1/2. This is the same ratio found in kaolin clays.

It is apparent from the above discussion that selection of a waste sludge composition as feedstock for alumina production may influence process cost. Thus, the sludge recommended for use as the feed to the alumina process in the baseline scheme analysis was that most closely representing the mean composition of the various sludges presented in Table 1. The lime sludge from the TVA Shawnee plant fits this criterion. (The selection was partially influenced by sludge characterization data availability and reliability.)

The sludge composition used as a base-case feed to the alumina process is that shown in the last row of data in Table 1. The composition of the selected waste sludge differs from the actual composition of the Shawnee lime sludge only in ash content. Because ash content and composition varies widely with fuel and because not all scrubbers utilize simultaneous SO_x - ash removal, it was decided that the base case engineering analysis should not include ash concentrations greater than those found in sludges generated from the SO_x removal of "particulate-free" FG. The ash content of the slurry can then be treated parametrically as an alumina/silica ratio in the sludge or as a clay composition variable.

BASE CASE PROCESS DESIGN DEVELOPMENT

This process for utilizing lime/limestone scrubber wastes in the extraction of alumina from clay is based on the following criteria:

1) Feedstock: Sulfur dioxide wet lime/limestone scrubber wastes sludge delivered by pipeline from a 1000 MW power plant co-loscated with the process plant. The feed sludge will contain 50 percent water and 50 percent solids with the following composition:

Sludge Composition, weight percent on dry basis

CaO	40.69
SO_2	34.72
SO_3	10.70
CO_2	2.2
Fixed Water	9.70
Fly Ash	2.0

Kaolin clay (containing 20 percent water) delivered by rail to the plant site from a local mine.

Clay Composition, weight percent dry basis

Al_2O_3	30
Fe_2O_3	3
SiO_2	50
LOI	15
Other	

Sodium carbonate delivered by rail from a local supplier

2) Plant location: Southeastern portion of U.S.A.

3) Reactions: The reactions of soda, alumina, calcium and silica will proceed to 96 percent completion given that these components exist in the following weight ratios:

$CaO/SiO_2 = 1.8$ and $Na_2O/Al_2O_3 = 1$

4) Steam: Steam for evaporators and autoclaves will be generated in waste heat boilers on the rotary kilns. Additional steam requirements will be met by combusting kiln off-gases and coal.

5) Process: Bituminous coal will be delivered by rail or transferred from a local mine and preparation plant.

Coal Composition

Moisture	1.5
Volatile Matter	26.7
Fixed Carbon	57.9
Ash	13.9
C	72.7
H	4.5

O	3.7
N	1.2
S	4.1
H.V.	13010 Btu/lb

6) Water: Plant water requirements are satisfied with water obtained from the sludge feedstock.

7) Effluents: Anticipated pollution control devices are included in the design and priced as units.

The plant design parallels the Bureau of Mines (BuMines) lime-soda-sinter process in which alumina is extracted from clay by sintering with soda ash and limestone[3]. The sinter is leached using a diluted sodium carbonate solution to form sodium aluminate solution. This solution is treated with lime to remove dissolved silica and then carbonated to precipitate alumina trihydrate. The trihydrate is calcined to α-alumina.

The TRW process is an adaptation of the BuMines lime-soda sinter process in that lime/limestone waste sludge from sulfur dioxide wet scrubber systems, as used in coal burning power plants, replaces limestone as a major feedstock. Sulfur and dicalcium silicate are recovered as by-products. The major benefit derived via the TRW concept is that it permits the processing of sulfur containing feedstocks.

The TRW process for utilization of lime/limestone wastes is separated into five sections: Feed Processing and Sintering, Dicalcium Silicate Extraction and Recovery, Desilication, Alumina Recovery and Soda Ash Recovery. Process flow diagrams for each of these sections are shown in Figures 2 through 6. Material balances are shown in Tables 2 and 3.

Feed Processing and Sintering

In the feed processing and sintering section (Figure 2) raw kaolin clay, lime/limestone scrubber waste sludge, sodium carbonate solution and recycled desilication residue are ground and blended in tube mills to prepare a mixture for sintering. The wet mixture is fed to indirect dryers where 250 psig steam is used to supply 7,000 MM Btu/D to drive off 6,326,000 lb/D of water, leaving

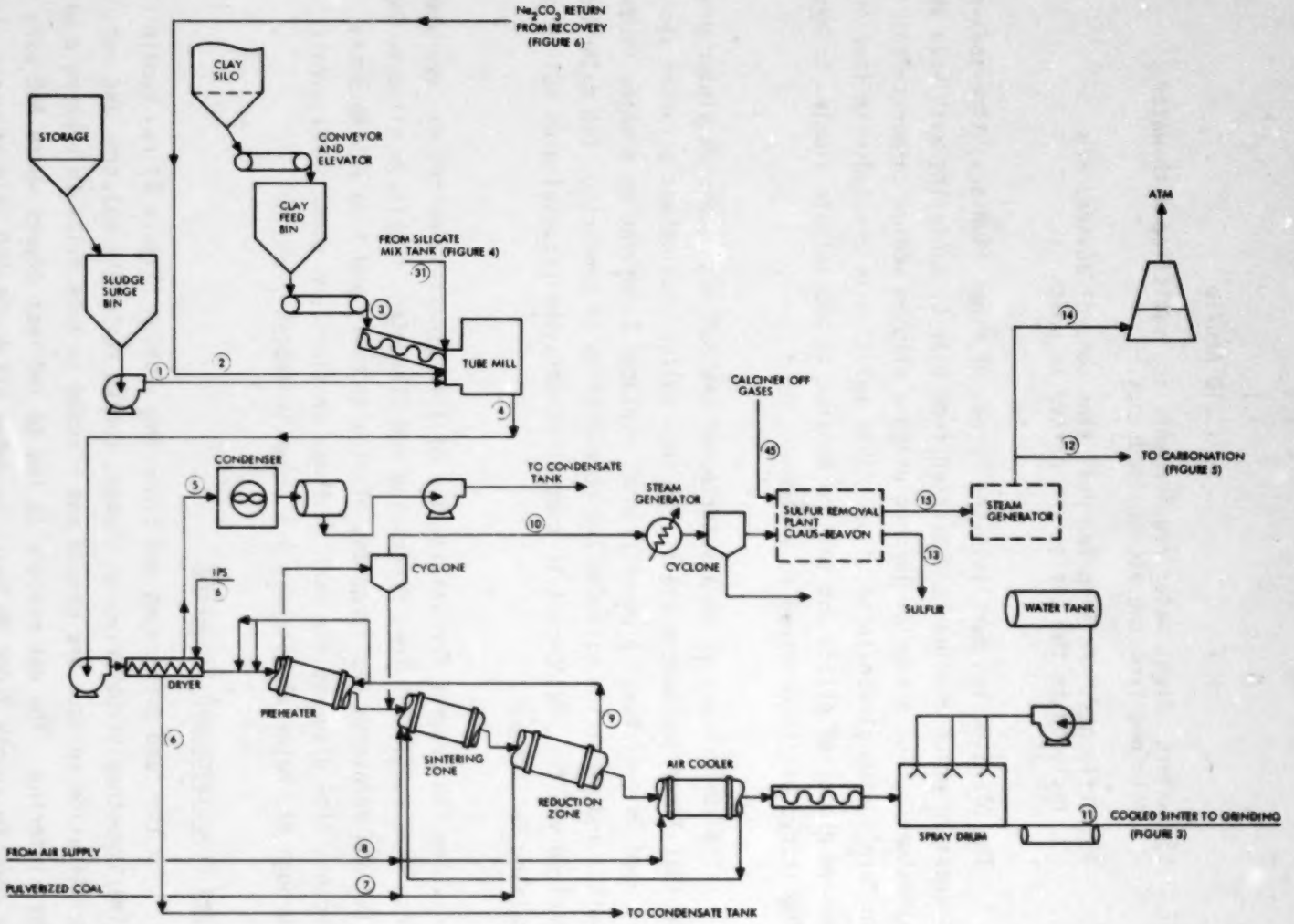

Figure 2. Feed Preparation and Sintering Section

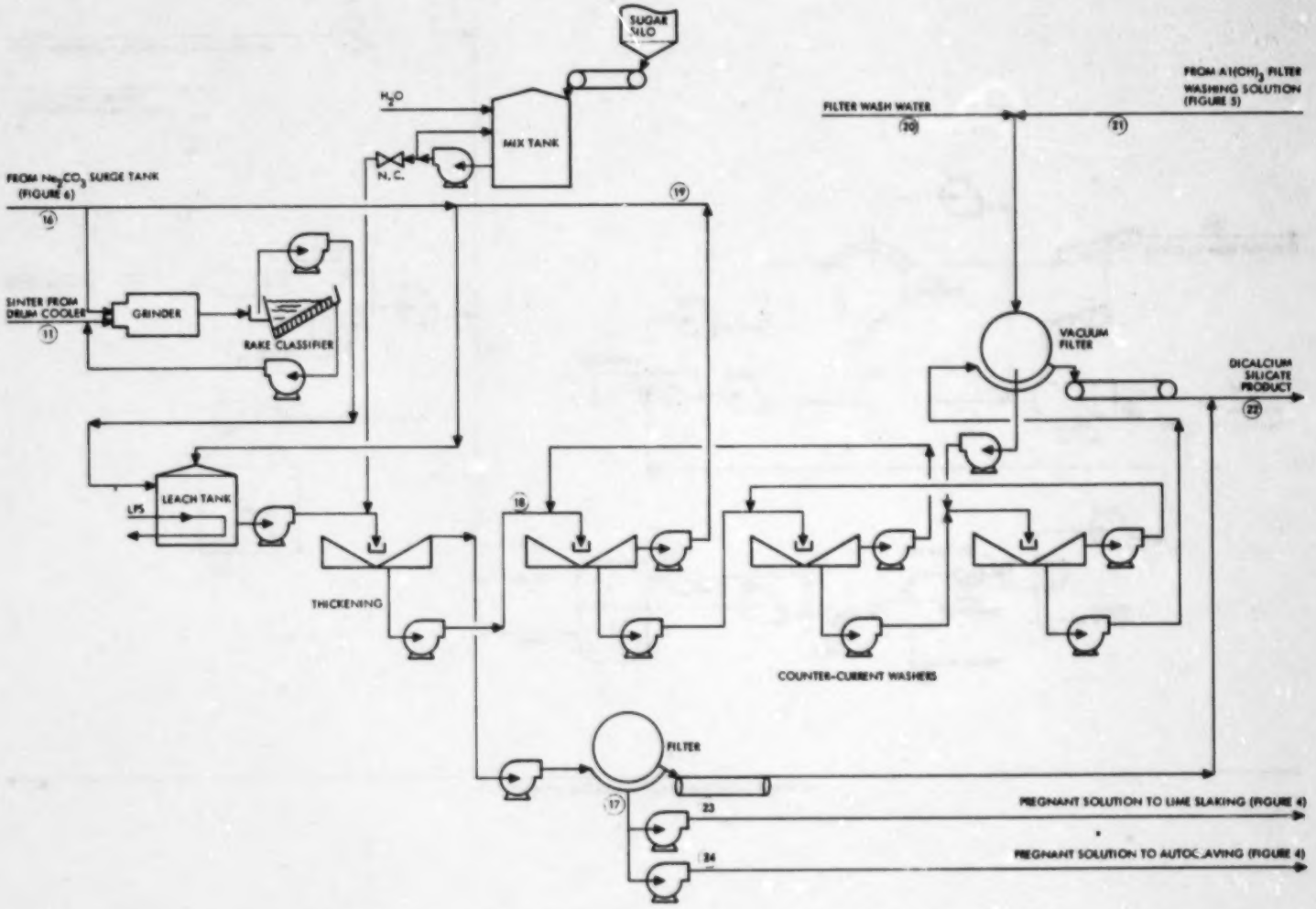

Figure 3. Dicalcium Silicate Extraction and Recovery Section

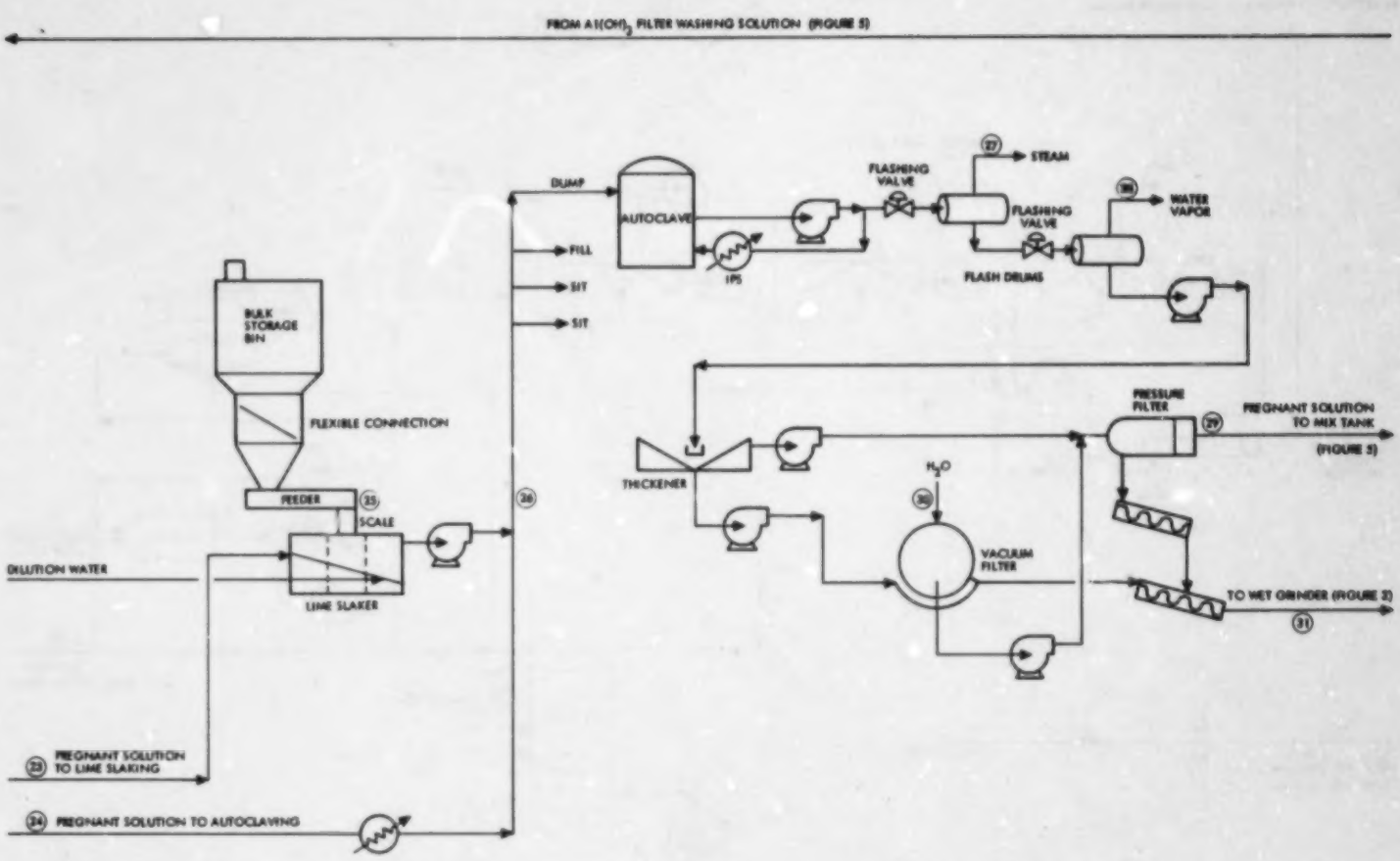

Figure 4. Desilication Section

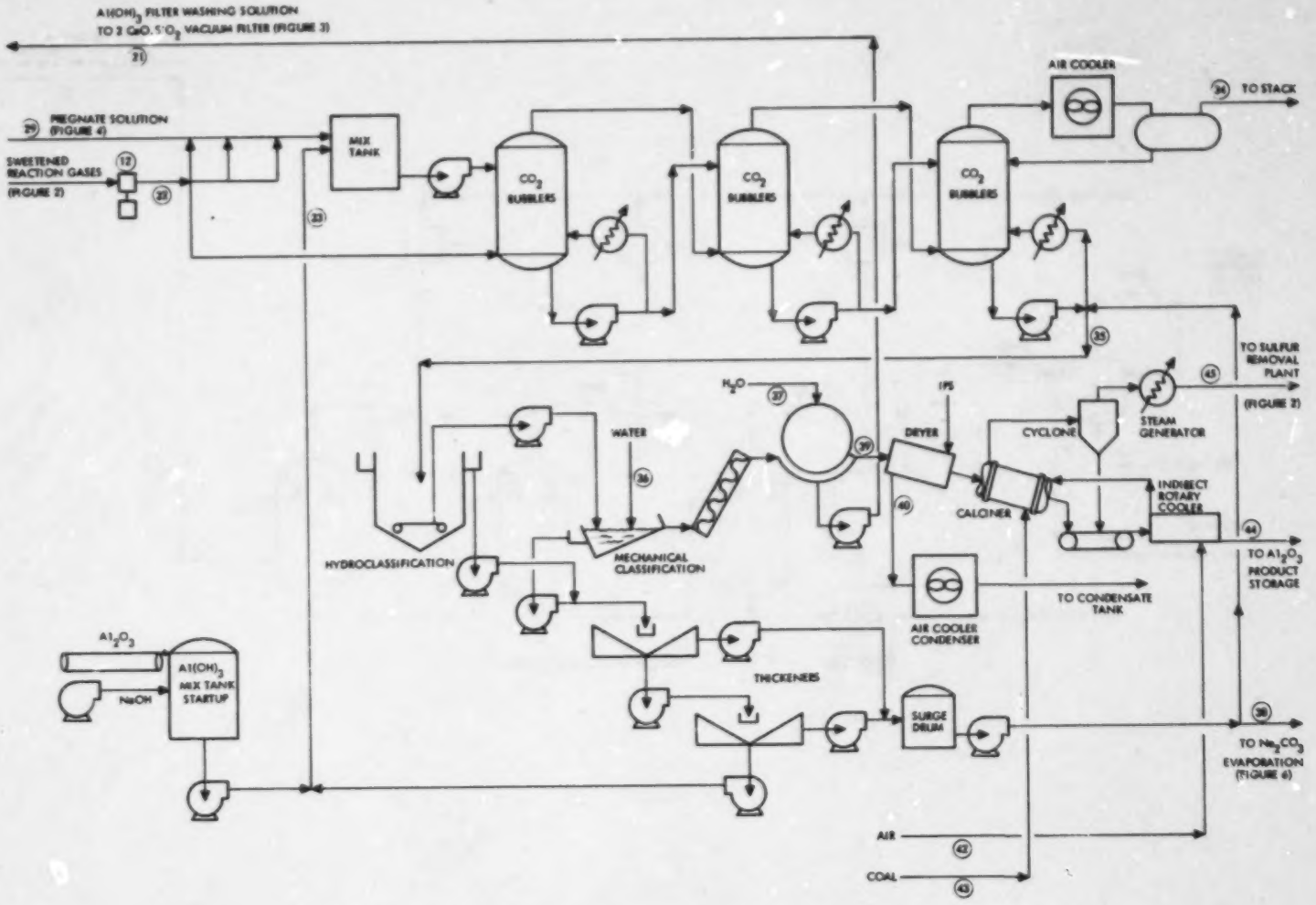

Figure 5. Alumina Recovery Sections

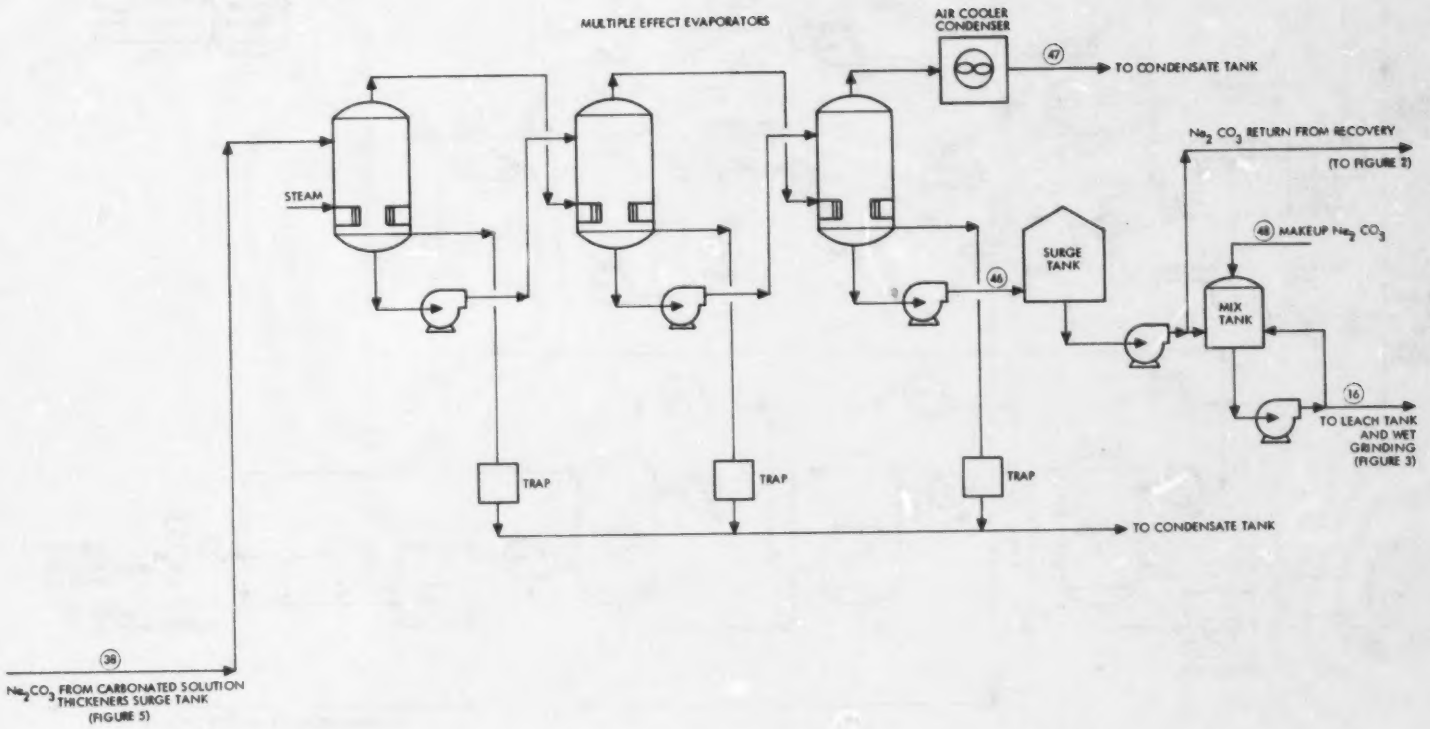

Figure 6. Soda Ash Recovery Section

TABLE 2. SINTERING AND REDUCTION ZONES
MATERIAL AND ENERGY BALANCE

Basis: 1 day, $T_{ref.}$ = 25°C

In	Lbs	HF at 780°C kcal/gmole	H MM Btu at 780°C (1436°F)
$Al_2O_3 \cdot 2SiO_2$	860,537	-722.1	- 5,035.2
$CaCO_3$	242,940	-248.4	- 1,085.2
Na_2CO_3	707,661	-237.8	- 2,858.4
$CaSO_4$	709,608	-329.5	- 3,091.5
$CaSO_3$	2,539,481	-267.2	-10,165.6
Fe_2O_3	45,340	-167.5	- 85.6
SiO_2	310,843	-204.9	- 1,907.6
$NaAlO_2$	225,248	-255.8	- 1,265.2
Ash and Other	109,030		+ 26.5
Coal	1,180,481	0.731 at room temperature	+ 173.9
Air	5,242,803	Preheated with solid effluents	+ 1,457.3
Total	12,173,971		-23,836.6

Out	Lbs	HF at 1200°C kcal/gmole	H MM Btu at 1200°C (2192°F)
$Al_2O_3 \cdot 2SiO_2$	46,648	-698.2	- 263.9
CaO	1,048,749	-139.4	- 4,693.2
Na_2O	186,724	-112.9	- 612.2
Ca_2SiO_4	867,785	-571.5	- 5,182.6
Fe_2O_3	45,340	-155.3	- 79.0
SiO_2	448,439	-198.2	- 2,662.9
$NaAlO_2$	825,930	-268.8	- 3,538.4
Ash and Other	271,935		+ 85.4
SO_2	594,303	- 72.9	- 1,216.6
H_2S	633,215	- 10.3	- 346.1
CO	859,740	- 18.9	- 1,045.9
CO_2	2,194,680	- 81.1	- 7,284.4
H_2	3,132	+ 7.9	+ 22.1
H_2O	111,955	- 49.4	- 552.1
N_2	4,035,396	+ 8.4	+ 2,165.1
Total	12,173,971		-25,204.7
Heat loss	(~6%)		+ 1,368.1
TOTAL			-23,836.6

TABLE 3. MATERIAL BALANCES

Stream No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
In M lbs/D	Sludge	Recycle Na_2CO_3	Clay	Slurry	Water Vapor	Drying Steam	Pulverized Coal	Air	Reduction Off-Gases	Sour Gases	Cooled Sinter	Carbonation Gases	Sulfur	Stack Gases	Sweeten Fuel Gases	Na_2CO_3 Leachate
Ash, etc.	78		30	109	2						277					17
Al_2O_3		52	453	535							530					
CaO	1,587			1,614							1,598					
Na_2O		481		499							494					204
CO_2	86	294		401												128
SiO_2		1	756	777							769					
Fe_2O_3			45	45							45					
H_2O	4,279	1,659	605	6,553	6,326	7,366					(541)					563
SO_2	1,354			1,354												
SO_3	417			417												
Total	7,801	2,487	1,889	12,304	6,238	7,366			29	27	4,220		895			912
Coal							1,180									
Air								5,243								
Gases																
H_2S									633	633						
SO_2									594	594						
CO									860	860					860	
CO_2									2,195	2,195		380		4,088	2,346	
H_2									3	3					2	
H_2O									112	339		80		481	924	
N_2									4,035	4,035		622		6,686	4,482	
Other												4		37		
Total									8,432	8,659		1,085		11,292	8,613	

TABLE 3. (CONTINUED)

Stream No.	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31
In M lbs/D	Pregnant Solution	Thickener Underflow	Leaching Solution	Filter Wash Water	Washing Solution	Dicalcium Silicate	Pregnant Solution	Pregnant Solution	Lime	Autoclave Feed	Steam	Water Vapor	Filtrate	Water	Silicant
Ash, etc.		277				277			1	1					1
Al_2O_3	509	241	203		4	42	51	458		509			479		30
CaO		1,613	15			1,598			27	27					27
Na_2O	716	340	357		51	33	72	644		716			698		18
CO_2	147	92	110		35	16	15	132		147			126		21
SiO_2	21	753	5			748	2	18	1	21			1		20
Fe_2O_3		45				45									
H_2O	4,834	2,370	6,100	3,409	1,401	1,080	483	4,351		4,834	309	254	4,380	120	10
SO_2															
SO_3															
Total	6,227	5,731	6,790	3,409	1,491	3,839	623	5,603	29	6,255	309	254	5,684	120	128
Coal															
Air															
Gases															
H_2S															
SO_2															
CO															
CO_2															
H_2															
H_2O															
N_2															
Other															
Total															

TABLE 3. (CONTINUED)

Stream No.	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48
M lbs/D	Sweetened Reaction Gases	Alumina Seed	Carbonation Gases	Alumina Solution	Water	Water	Na_2CO_3 Solution	Alumina Trihydrate	Condensate	Steam	Air	Coal	Al_2O_3	Calciner Off-Gases	Concentration Na_2CO_3 Solution	Condensate	Makeup Na_2CO_3
Ash, etc.																	
Al_2O_3		115		594			69	405					401		69		
CaO																	
Na_2O		30		727			644	2					2		644		41
CO_2		17		446			393	1					1		393		29
SiO_2				1			1								1		
Fe_2O_3																	
H_2O		273		4,630	1,053	812	4,399	424	209	274					2,222	2,257	
SO_2																	
SO_3																	
Total		435		6,398	1,053	812	5,506	833	209	274			404		3,329	2,257	70
Coal												56					
Air											582						
Gases																	
H_2S																	
SO_2														5			
CO																	
CO_2	380		77											151			
H_2																	
H_2O	80		103											238			
N_2	622		622											447			
O_2			3											6			
Other	3													8			
Total	1,085		805											846			

the chemically fixed water in the clay. The remaining 227,000 lb/D of fixed water is driven off in the preheaters where 1200°C (2192°F) reduction zone off-gases are used to supply 1993 MM Btu/D to raise the mixture temperature to 780°C (1436°F). No sulfur compounds are expected to decompose here. The mixture is next reacted in an atmosphere produced by burning coal at 1200°C (2192°F) with less than the stoichiometrically required amount of air. Along with the reactions associated with the combustion of coal, the following chemical reactions are assumed to occur:

$$Al_2O_3 \cdot 2SiO_2 + 4CaSO_4 + Na_2CO_3 + 8CO + 8H_2 \rightleftarrows 2NaAlO_2 + 2Ca_2SiO_4 + 4H_2S + 9CO_2 + 4H_2O \quad (1)$$

$$Al_2O_3 \cdot 2SiO_2 + 4CaSO_3 + Na_2CO_3 + 8CO + 4H_2 \rightleftarrows 2NaAlO_2 + 2Ca_2SiO_4 + 4H_2S + 9CO_2 \quad (2)$$

$$Na_2CO_3 \rightleftarrows Na_2O + CO_2 \quad (3)$$

$$CaSO_3 + CO + 2H_2 \rightleftarrows CaO + H_2S + CO_2 + H_2O \quad (4)$$

$$CaSO_4 + CO + 3H_2 \rightleftarrows CaO + H_2S + CO_2 + 2H_2O \quad (5)$$

$$CaCO_3 \rightleftarrows CaO + CO_2 \quad (6)$$

$$H_2S + O_2 \rightleftarrows SO_2 + H_2 \quad (7)$$

$$H_2O + CO \rightleftarrows CO_2 + H_2 \quad (8)$$

$$2H_2 + O_2 \rightleftarrows 2H_2O \quad (9)$$

The amount of air supplied was determined so as to obtain the gaseous products in the following proportions:

$H_2S:SO_2 = 2:1$

$H_2:H_2O = 1:4$

and $\dfrac{[CO_2][H_2]}{[CO][H_2O]} \sim .4$

If a 2:1 molar ratio of H_2S to SO_2 can be obtained in the kilns, the Claus unit furnace is not required. The mass and energy balances for the sintering and reduction kilns are shown in Table 2. The reduction zone off-gases are used to preheat the solids entering the sintering kiln. In doing so, the gas temperature drops to about 704°C (1300°F). The hot gas is then used to generate some 1,794,000 lb/D of 250 psig steam before the temperature is lowered to 232°C (450°F), a temperature at which it can join the 232°C (450°F) gases from alumina trihydrate calcination in the first Claus converter.

The sulfur plant is a Claus unit, minus a furnace and waste heat boiler, coupled with a Beavon tail gas plant. The units are sized to produce 400 long tons per day of sulfur. The steam requirement on the Claus plant is that required to reheat the gas from the first condenser before it is fed to the second converter. All the boiler feedwater for this plant is heated to 93°C (200°F) in cooling coils on the two sulfur condensers of the Claus plant. The sweetened gases are burned in a low Btu boiler which generates 3860 MM Btu of 250 psig steam. A percent of the combustion products is used for carbonation.

Solid products from the reduction zone kiln are cooled to 60°C (140°F) in preheating the air used for combustion. These solids are then wetted to facilitate conveyance of the next section.

Several assumptions were made in the feed preparation and sintering sections, the viability of which can be tested only in a laboratory. The first assumption was that the hydrogen and carbon monoxide required by the quasi-sintering reactions, reactions (1) and (2), could be produced by combustion of coal with less than the stoichiometrically required air in a rotary kiln. The process may require a coal gasification reactor for some, or all of the coal required in the reactions. The second assumption was that the proper order for the reactions was sintering first, bringing the materials to reaction temperatures, and then reduction to convert most of the sulfur produced to hydrogen sulfide. It may be that the correct order is just opposite to that assumed. The third assumption was that the amount of air calculated would produce a product similar to that from a Claus furnace. It may be that almost

all of the sulfur produced in the kilns will be in the form of hydrogen sulfide. If so, H_2S will be separated from the other gases in an absorption plant and then converted to sulfur using a traditional Claus process.

Dicalcium Silicate Extraction and Recovery Section

In the dicalcium silicate extraction and recovery section (Figure 3), the cooled, wet sinter, containing 530,000 lb/D of alumina, proceeds through a grinder/rake classifier section to the sodium carbonate leach tanks. A portion of the recovered sodium carbonate solution is added to the grinder and the remainder is pumped to the 60°C (140°F) sodium carbonate leach tank. The leach tanks were sized for a 30 minute capacity. The leach tank effluent is pumped to a thickener where the pregnant solution is separated from the dicalcium silicate slurry. The thickener has a settling area of 1.7 square feet per ton of dry solids per day. The pregnant solution, thickener overflow, is pumped to a filter. The filter residue is added to the dicalcium silicate product. The filtrate is pumped to the desilication section. A sugar solution is available for pumping to the thickener in case the solution gels. The thickener underflow is washed countercurrently in three thickeners. Overflow from the first thickener is recycled to the leach tank. Overflow from the second thickener is used as wash solution for the first and overflow from the third thickener is wash solution for the second. Underflow from the third thickener is vacuum filtered. The three thickeners have settling areas of about 3.2, 3.4, and 3.5 square feet per ton of dry solids per day respectively. Approximately 1,491,000 lb/D of recovered washing solution from the alumina trihydrate filter in the alumina recovery section is used as wash solution for this vacuum filter. Recovered solution is used as wash for the third thickener. The filter residue is 3,843,000 lb/D of dicalcium silicate product which is sent to product storage and later to a cement manufacturing plant where it replaces most of the lime and silica feedstocks.

Desilication Sections

The pregnant solution from the dicalcium silicate recovery section (Figure 4) is divided so that about 10 percent of the stream is used for slaking lime. The other 90 percent is preheated to 199°C (390°F), mixed with the cool

lime containing solution and sent to one of five batch autoclaves to be held at 177°C (350°F) and 100 psig for 2 hours. Most of the silica in solution reacts to form a precipitate assumed to be $2Na_2O \cdot 2Al_2O_3 \cdot 3SiO_2 \cdot 5H_2O$. Six percent of the alumina and three percent of the soda in solution also precipitate along with the silica. The slurry from the autoclave is sequentically flashed at 30 psig and then at atmospheric pressure. Approximately 309,000 lb/D of 30 psig steam is recovered from the first flash vessel. The pregnant solution is then separated from the desilication residue in a five foot per ton of dry solids surface area thickener. Underflow from the thickener is washed and vacuum-filtered. Almost 128,000 lb/D of filtered desilication residue is recycled to the wet grinder in the feed preparation and sintering section of the plant. Filtrate from the vacuum filter and overflow from the thickener are pumped through pressure leaf filters to the mix tank in the alumina recovery section. Residue from the leaf filters is added to recycled desilication residue or sent to solids disposal.

Alumina Recovery Section

In the alumina recovery section (Figure 5) flue gases from the calcining kiln are bubbled into the desilicated solution as it is pumped to the mix tank. To promote precipitation, 434,391 lb/D of alumina trihydrate seed, about 25 percent of the alumina that precipitates, is added to the mix tank. The solution is then pumped through three stages of carbonation where flue gases from the steam generation are used to reduce the solution pH to the level required for aluminum trihydrate precipitation. About 86 percent of the alumina in the desilicated liquor precipitates according to the following reaction:

$$Na_2O \cdot Al_2O_3 + CO_2 + 3H_2O \rightarrow Al_2O_3 \cdot 3H_2O + Na_2CO_3 \qquad (10)$$

The slurry from the final stage of carbonation is pumped to hydroclassification and mechanical classification. Overflow from classification contains aluminum trihydrate fines which are recovered in two thickeners and recycled to the mix tank as seed. Overflow from the fine aluminum trihydrate thickeners are pumped to a sodium carbonate solution surge drum. Approximately 30 percent of the sodium carbonate is recycled to hydroclassification. The remaining 5,587,017

lb/D of solution is pumped to the soda ash recovery section. Coarse aluminum trihydrate is contained in the classifier underflow and is filtered and washed in drum filters. Twenty-five percent of the filter cake material is free water which is removed with 250 psig steam in an indirect dryer. The dried material, 624,238 lb/D, is calcined at 1093°C (2000°F) to α-alumina. The calcination reaction is shown in equation (11):

$$Al_2O_3 \cdot 3H_2O \rightarrow Al_2O_3 + 3H_2O \qquad (11)$$

the product has the following composition:

	Weight Percent
Al_2O_3	99.25
Na_2O	.50
CO_2	.25
	100.00

Soda Ash Recovery Section

The soda ash recovery section (Figure 6) consists of triple effect evaporators. Thickener overflow from the carbonated solution surge tanks is concentrated in the evaporators. About 75 percent of the evaporator effluent goes to the feed preparation and sintering section. The remainder is reconcentrated with makeup soda ash in the mix tank before being pumped to the dicalcium silicate extraction and recovery section.

BASE CASE PROCESS CAPITAL AND OPERATING COSTS

Presented in this section are estimates of the total plant investment and annual operating cost requirements for the conceptualized TRW alumina extraction process. Cost of major processing equipment are itemized by processing section. The related economics for portland cement manufacture are presented in this section. All costs are quoted at a Marshall and Stevens index of 444.3, the annual index for 1975. Raw materials and land costs are not included in the investment estimates.

Two differing methods of plant investment and capital cost estimation are represented in Tables 4 and 5. The method illustrated in Table 4 has been

TABLE 4. TOTAL ESTIMATED CAPITAL REQUIREMENTS*
(BuMines Method)

	Millions $
Feed Preparation & Sintering†	24
Dicalcium Silicate Extraction	2
Desilication	1
Alumina Recovery	4
Soda Ash Recovery	0.2
Pumps @ 4% of above	1
Total Installed Equipment Cost	32.2
Steam Plant	0.3
Subtotal	32.5
Plant Facilities, 10% of Subtotal	3
Plant Utilities, 12% of Subtotal	4
Total Construction	39.5
Initial Catalyst Requirement	§
Total Plant Cost	39.5
Interest During Construction	7
Subtotal for Depreciation	46.5
Working Capital	5
Total Investment	51.5

* BuMines Format

† Includes Sulfur Recovery Plant

§ Included in Sulfur Recovery Plant

TABLE 5. TOTAL ESTIMATED CAPITAL REQUIREMENTS*
(TVA Method)

	Millions $
Feed Preparation & Sintering†	24
Dicalcium Silicate Extraction	2
Desilication	1
Alumina Recovery	4
Soda Ash Recovery	0.2
Pumps	1
Total Installed Equipment Cost	32.2
Steam Plant	0.3
Subtotal	32.5
Plant Facilities, Plant Utilities } 5% of Subtotal	2
Subtotal Direct Investment	34.5
Engineering Design and Supervision	3
Construction Field Expense	3
Contractor Fees	2
Contingency	3
Subtotal Fixed Investment	45.4
Interest During Construction	4
Working Capital	2
Total Capital Investment	52.5

* TVA format

† Includes Sulfur Recovery Plant

used by BuMines in all investigations of alumina extraction processes to date and is of the general type called "study estimate"[6]. This "study estimate" technique has been used herein so that comparisons may be made with BuMines figures. A more conventional method of presenting capital estimates is shown in Table 5[7]. As may be observed, the latter method results in an approximate 0.2 percent increase. The impact of this increase upon alumina selling prices and sludge credits is insignificant (see discussion of raw material and product value).

Table 6 presents the utility requirements for steam, coal and water. Cost estimates for utilities and facilities, Table 4, are taken as 12 percent and 10 percent of the total physical cost, respectively. These percentages are based upon a plant complexity level of four as delineated in the Oil and Gas Journal cost estimating methodology, 22 July 1974. Included under plant utilities are fire protection equipment, refrigeration, gas, power and water distribution, etc. Plant facilities include administration buildings, warehouses, shops, laboratories, etc. Utility and facility costs as shown in Table 5 are taken as five percent of the direct investment subtotal.

The sulfur removal plant consists of a combination of Claus and Beavon units. The cost quoted in Table 7 is for both units and is based upon a daily production of 382 long tons of sulfur. Tables 8 through 11 summarize the individual equipment costs for the other various process sections.

Working capital as shown in Table 4 is taken as 10 percent of the total plant cost plus interest during construction. Interest during construction is calculated as the product of interest rate, total plant cost and construction time. Interest rate is taken as nine percent and construction time as two years. The total plant investment, so calculated, is $51.5 million.

The working capital of Table 5 is calculated as the equivalent of: three weeks, raw material; seven weeks, direct cost; and seven weeks, overhead. Interest during construction is calculated over the construction period at eight percent with 75/25 debt-to-equity ratio. Total plant investment via this method is $52.5 million.

TABLE 6. DAILY PLANT UTILITY REQUIREMENTS

	Steam, M lbs								Waste Heat		Plant Water	Cooling Water	Coal	Electric Power
	250 psig Steam		100 psig Steam		30 psig Steam		5 psig Steam		MM Btu/D		M Lb/D	M Lb/D	MM Btu/D	kwhr/hr
	Consumed	Produced	Consumed	Produced	Consumed	Produced	Consumed	Produced	Consumed	Produced				
Feed Preparation and Sintering Section											4300			
Dryers	7366								1993	1993	227			
Preheaters											-541		15358	
Kilns		1794										6886		332.5
Claus Converters and Condensors	205					239					-398			49.9
Beavon														
Dicalcium Silicate Extraction and Recovery Section														
Steam tracing on pipes,							138				-3409			
filters, tanks, etc.											309			
Desilication Section											254			
Heat Exchangers					325	309					120			
Autoclaves	946										-1866			
Alumina Recovery Section														
CO_2 Bubblers											209			
Dryers	275						inc.						713	
Calciners		419												
Soda Ash Recovery											2257			
Evaporator, three effect			1328										4249	
Steam Generator*		6579		1328										
Theoretical Totals	8792	8792	1328	1328	325	549	138	0	1993	1993	1224	6886	20320	382.4

* The 6,215,000 lbs of 250 psig steam is generated by combustion of reduction zone off gases, 3,797,000 lbs, and by combustion of coal, 2,418,000 lbs. The steam is generated at 250 psig and reduced to the pressures required.

TABLE 7. FEED PREPARATION AND SINTERING SECTION
EQUIPMENT LIST - MAJOR ITEMS

Item	No.	Cost	Unit Dimension*
Sludge Storage Bin	1	$ 176,000	643,000 gallons
Sludge Surge Bin	1	28,000	96,000 gallons
Clay Silo	1	86,000	188,000 gallons
Clay Feed Hopper	1	1,000	28,000 gallons
Conveyors	4	84,000	100'x24"(1), 30'x18"(1), 60'x18"(2)
Tube Mills	8	1,540,000	10' x 18'
Dryer	2	395,000	24,500 ft^2
Kilns - Preheat, Sinter & Reduction	6	5,046,000	
Kilns - Drum Cooler Conveyor	2	35,000	
Rotary Drum Coolers	2	450,000	
Beavon Plant	1	4,988,000	
Claus Plant†	1	3,640,000	399 Long Tons S/day
Total -			
as Purchased		16,469,000	
installed		24,209,000	

* Where dimensions are not given, costs are based on BuMines estimates.

† Does not include waste heat boiler or incinerator.

TABLE 8. DICALCIUM SILICATE EXTRACTION AND RECOVERY SECTION EQUIPMENT LIST - MAJOR ITEMS

Items	No.	Cost	Unit Dimension*
Tube Mills	2	$ 385,000	
Rake Classifiers	2	41,000	
Leach Tanks	2	13,000	12,000 gallons
Thickener No. 1	1		3,800 ft^2
Thickener No. 2	1	296,000	6,200 ft^2
Thickener No. 3	1		6,500 ft^2
Thickener No. 4	1		6,800 ft^2
Sugar Silo & Mix Tank		25,000	
Rotary Vacuum Filters	2	128,000	
Conveyors (screw)	2	24,000	60' x 12"
Total -			
as Purchased		912,000	
installed		1,881,000	

* Where dimensions are not given, costs are based on BuMines estimates.

TABLE 9. DESILICATION SECTION
EQUIPMENT LIST - MAJOR ITEMS

Items	No.	Cost	Unit Dimension*
Lime Slaking Storage Bin	1	$ 4,000	3,600 gallons
Lime Slaker & Feeder	1	5,000	
Autoclaves	5	535,000	10,000 gallons
Flash Tanks	2	11,000	8,500 gallons
Thickener	1	16,000	300 ft^2
Rotary Vacuum Filter	2	38,000	
Pressure Leaf Filter	2	38,000	
Screw Conveyors	2	37,000	100' x 12"
Totals -			
as Purchased		684,000	
installed		1,253,000	

* Where dimensions are not given, costs are based on BuMines estimates.

TABLE 10. ALUMINA RECOVERY SECTION
EQUIPMENT LISTS - MAJOR ITEMS

Items	No.	Cost	Unit Dimension*
$Al(OH)_3$ Seed Tank & Agitator	1	$ 8,000	6,700 gallons, 10 H.P.
Carbonators	3	48,000	100,000 gallons
Hydroclassifier	1	15,000	
Rake Classifier	1	11,000	
Thickener	1	62,000	
Surge Drum	1	11,000	20,000 gallons
Mix Tank (pre-carbonation)	1	13,000	25,000 gallons
Screw Conveyor	1	9,000	30' x 14"
Dryer ($Al_2O_3 \cdot 3H_2O$)	1	100,000	
Kiln (calcination)	1	1,088,000	
Indirect Rotary Cooler	1	296,000	
Combustion Gas Scrubber	1	442,000	
Cyclone	2	13,000	
Rotary Vacuum Filter	1	49,000	
Totals -			
as Purchased		2,165,000	
installed		3,565,000	

* Where dimensions are not given, costs are based on BuMines estimates.

TABLE 11. SODA ASH RECOVERY SECTION
EQUIPMENT LIST - MAJOR ITEMS

Items	No.	Cost	Unit Dimension*
Na_2CO_3 Mix Tank	1	$ 61,000	87,000 gallons
Na_2CO_3 Surge Tank	1	38,000	32,800 gallons
Triple Effect Evaporator -	1		
Stage 1		3,000	2,000 gallons
Stage 2		4,000	2,800 gallons
Stage 3		4,000	4,000 gallons
Total -			
as Purchased		110,000	
installed		228,000	

* Where dimensions are not given, costs are based on BuMines estimates.

Purchased equipment costs are estimated from various textbook sources including a detailed BuMines analysis of the lime-soda-sinter process for the extraction of alumina from kaolin clay[3]. In particular, the ratios necessary to compute installed versus purchased equipment costs for the various process sections are taken from this reference which closely parallels the TRW process. Installed equipment costs reflect charges for foundations, buildings, and structures, insulation, instrumentation, electrical, piping, painting and miscellaneous fixtures.

The operating costs presented in Table 12 also follow a BuMines format. Estimates of capital investment and operating expense for a cement plant producing 858,000 tons per year (350 days) are itemized in Table 13. These costs are updated from a previous TRW publication[5].

TABLE 12. ESTIMATED ANNUAL OPERATING COST

	Annual Cost (Thousands)	Cost per Ton Alumina
Direct Cost:		
Raw Materials:		
Lime at $35/ton	$ 173	$ 2.46
Coal at $20/ton	5,466	77.90
Clay at $ 6/ton	1,905	27.14
Soda ash at $47/ton	576	8.20
Total	8,120	115.70
Utilities:		
Fuel gas at $2.00/MM Btu	175	2.49
Electric power at 4 cents/KW-hr	1,599	22.78
Water, Beavon plant, at 20 cents/M gal	14	.20
Total	1,787	25.47
Direct Labor:		
Labor at $6.00/hr	842	12.00
Supervision, 15 pct of labor	126	1.80
Total	968	13.80
Plant Maintenance		
Labor at $15,000/yr	705	10.50
Supervision, 20 pct of labor	141	2.01
Materials and Contracts	1,058	15.07
Total	1,094	27.13
Payroll Overhead	544	7.76
Operating Supplies	381	5.42
Total Direct Cost	13,703	195.25
Indirect, overhead	1,301	18.54
Fixed Costs:		
Taxes, Insurances	759	10.82
Depreciation	2,349	33.45
Total, before credits	18,112	258.07
Credits:		
Dicalcium Silicate @ $1.00/ton	652	9.30
Sulfur @ $10.00/ton	1,563	22.27
Sludge removal @ $5.00/ton	6,825	97.26
Total Operating Cost	$ 9,072	129.24

TABLE 13. ESTIMATED ECONOMICS OF PORTLAND CEMENT MANUFACTURE*

Installed Capital Investment (4.5 MM bbl/yr)	$ 35.2 MM
Operating Costs (annual)	Thousands $
Direct Costs	
Limestone ($6/ton)	2,247
Dicalcium Silicate ($1/ton)	652
Gypsum ($10.00/ton)	456
Coal ($2.00/MM Btu)	11,992
Electrical Energy ($0.04/KWh)	1,030
Water ($0.08/gal)	46
Operating Labor†	867
Supervision and Benefits	867
Maintenance and Supplies (4% of Invest./yr)	1,094
Total Direct Costs	19,251
Indirect Costs	
Depreciation (5%/yr)	1,369
Interest (at 7%, 20% debt)	411
Insurance and Local Taxes	821
Overhead	1,049
Total Indirect Costs	3,650
Total Manufacturing Cost	$22,901

* Wet process plant

† 28 men/shift

RAW MATERIAL COST AND PRODUCT VALUE

The present market price for alumina, as quoted in the Chemical Marketing Reporter for 26 July 1976, is $158 per ton. Because aluminum is the most abundant metallic element in the earth's crust, has universal application in production, and is the object of intense efforts on behalf of the aluminum industry to expand and develop markets, this commodity will continue to maintain its value and be a major growth metal for many years. Average annual growth rate[8] for demand is estimated to be in the range of 5.1 to 7.4 percent through the year 2000. This range corresponds to a U.S. demand in the year 2000 of from 21.2 to 42.0 million tons. These values may be compared with the actual 1968 demand of 4.31 million tons.

Nonmetallic usage of alumina is minimal at approximately 11 percent of total usage and is principally in the areas of refractories, chemicals and abrasives. The metallic uses are outlined as shown in the following:

Metallic Uses of Aluminum

Area	Percentage
Construction	24.6
Transportation	17.2
Electrical	11.8
Cans & Containers	14.1
Appliances	8.6
Machinery	5.7
Other	6.6
	88.6

Approximately 80 percent of the free world productive capacity for bauxite, alumina and aluminum is concentrated in six corporate groups or subsidiaries. These include one Canadian company, Alcan Aluminum Ltd.; three U.S. companies, ALCOA, Reynolds and Kaiser; and two French firms, Péchina, and Ugine. All companies are integrated in that they encompass the manufacturing process from mining of bauxite to finished aluminum products.

A conservative value of $10 per ton was used in base case assessments for sulfur by-product credit. Assessment of present market values for crude bright sulfur shows a range of $60 to $66 per ton. This commodity is subject

to rapid fluctuation; however, a continued strong demand is projected[9]. Lime-sulfur sludges are recognized as a tremendous reservoir of sulfur which is not significantly tapped at present. Sulfur during 1975 production totaled 10 million long tons, 76 percent of which was Frasch sulfur. The remaining production was from sour gas. Sulfur is currently in a somewhat short supply.

Principal usage of sulfur is in the following areas:

Area	Percent
Sulfuric Acid Manuf.	80
Pulp and Paper	5
Carbon Disulfide	2.5
Agriculture	1
Other	3.5

Major suppliers of sulfur as produced via the Frasch process are identified as follows:

Atlantic Richfield Co., Fort Stockton, Texas
Freeport Minerals Co., Chauvin, La.; Grand Isle, La;
Port Sulphus, La.; Venice, La.
Occidental Chemical Co., Long Point Dome, Texas
Texasgulf, Inc., Beaumont, Texas; Bullycamp Dome, La.;
Hampshire, Texas; Liberty, Texas; Newgulf, Texas

Refinery or natural gas producers are numerous. Therefore it is not expected that sulfur from FGD would have a significant influence upon market prices.

Dicalcium silicate, as produced in this process, has no established market. This material is an ideal feedstock for cement manufacture. Preliminary estimates are on the order of $1-2 per ton. A $1.0 per ton estimate was used in this assessment.

Clay feedstock will vary in price depending on locale and whether or not the material is self-mined, or contracted out and the type of mining required. Published market prices for refined kaolin clay do not apply to the raw material as mined and used in this process. A conservative range would be $4 to $8 per ton. A $6 per ton cost was used in this analysis, however, the price could conceivably be as low as $3 per ton. Sodium carbonate (Soda Ash) was taken at present market value, $47 - $49 per ton. In large quantities,

such as employed in this process, a contracted value may be significantly lower. Coal costs are somewhat volatile and subject to negotiation. Many present power facility contracts are based on coal prices in the $30 per ton range. However, these prices for a number of facilities were negotiated at a time of energy panic and will probably drop again. National Coal Association figures from the 1974 edition of Steam Electric Plant Factors indicate an approximate range for the Georgia region, as burned, at $9.07 - $11.46 per ton. Under inflation, this range would be $12.14 - $15.34 per ton in 1976. Coal prices are subject to quantity and negotiation. As such, it is difficult to fix a future price. For the purposes of this analysis $20 per ton was chosen.

PARAMETRIC EVALUATION OF COST SENSITIVITY

Alumina selling price is a function of several primary cost factors including raw material feedstocks, by-product credits, energy requirements, capital investment and total operating costs. In addition, the rate of return on investment is a determining factor. These relationships are characterized by the set of linear equations illustrated in Appendix B which relate the various economic variables at several discounted cash flow (DCF) rates. This evaluation consists of alternate cases in which alumina selling price and sludge credit are taken as dependent variables for the equations noted. In each specific case a different set of primary cost factors is postulated and either alumina selling price or sludge credit are calculated to match investment return rates of 10, 12 and 15 pct. discounted cash flow. In all cases where sludge credit (a negative expense) is defined as the independent variable, alumina price is fixed at $150 per ton. In cases where alumina selling price is the independent variable, sludge credit is fixed at $5 per wet ton (2000 lbs) or varied to assess the impact upon alumina price for a given set of cost factors. A utility financing value for selling price or credit based upon a 75/25 equity-to-debt ratio and an income tax rate of 48 percent is also included for each case. Table 14 presents the results of this analysis and series to illustrate the methodology.

Of primary interest are cases 13 and 14 in which the capital and operating costs for a combined cement and alumina plant are considered. The alumina selling price calculated for a $5 per ton sludge credit is $124 per

TABLE 14. ALUMINA SELLING PRICE AND SLUDGE CREDIT AS A FUNCTION OF PRINCIPAL ECONOMIC FACTORS

Basis for Price Estimation														Estimated Price of Alumina or Sludge							
														Utility Financing		10% DCF		12% DCF		15% DCF	
Case	Coal Cost	Clay Cost	Na_2CO_3 Cost	Capital Cost*	Capital Cost Cement Plant	Sludge Credit (wet basis)	Sludge Water Content	Alumina Credit	Dicalcium Silicate Credit	Cement Credit	Sulfur Credit	Alumina Plant Operating Costs†	Cement Plant Operating Costs	Alumina§ Selling Price	Sludge Credit	Alumina Selling Price	Sludge Credit	Alumina Selling Price	Sludge Credit	Alumina Selling Price	Sludge Credit
1 Base Case	$20	$ 6	$47	$52 MM	-	$ 1 5 10	50%	-	$1	-	$10	$18 MM	-	$297 218 122		$370 292 195		$404 327 229		$461 383 286	
															$ 8.57		$12.32		$14.08		$16.99
2	20	6	47	52 MM	-	-	50%	150	1	-	10	18 MM	-		6.59		10.34		12.10		15.00
3	10	6	47	52 MM	-	-	50%	150	1	-	10	15 MM	-		8.57		12.32		14.08		16.99
	20											18 MM			9.59		13.34		15.10		18.01
	25											19 MM			12.60		16.34		18.11		21.01
	40											24 MM									
4	20	6	47	52 MM	-	-	50%	150	1	-	10	18 MM	-		8.57		12.32		14.08		16.99
				X 0.5											6.29		7.21		8.08		9.49
				X 1.5											10.85		17.43		20.08		24.48
5	20	6	47	52 MM	-	5	50%	-	1	-	10	18 MM	-	218		292		327		383	
				X 0.5										175		193		210		237	
				X 1.5										264		392		444		529	
6	20	1	47	52 MM	-	5	50%	-	1	-	10	16 MM	-	197		270		304		360	
		6										18 MM		218		292		327		383	
		10												238		310		345		401	
7	20	1	47	52 MM	-	-	50%	150	1	-	10	16 MM	-		7.41		11.16		12.92		16.82
		6										18 MM			8.57		12.32		14.08		16.99
		10													9.50		13.18		15.01		17.92

* Alumina + Sulfur Plant

† Before credits, includes sulfur plant

§ Units: $/ton (2000 lbs)

TABLE 14. (CONTINUED)

Case	Basis for Price Estimation: Coal Cost	Clay Cost	Na_2CO_3 Cost	Capital Cost*	Capital Cost Cement Plant	Sludge Credit (wet basis)	Sludge Water Content	Alumina Credit	Dicalcium Silicate Credit	Cement Credit	Sulfur Credit	Alumina Plant Operating Costs†	Cement Plant Operating Costs	Estimated Price of Alumina or Sludge — Utility Financing: Alumina Selling Price‡	Utility Financing: Sludge Credit	10% DCF: Alumina Selling Price	10% DCF: Sludge Credit	12% DCF: Alumina Selling Price	12% DCF: Sludge Credit	15% DCF: Alumina Selling Price	15% DCF: Sludge Credit
8	20	6	47	$1 MM	-	9	10%	-	1	-	10	15 MM	-	$201		$271		$304		$360	
				$2 MM		5	50%					18 MM		218		292		327		383	
				$4 MM		2.50	75%					20 MM		256		332		367		426	
9	20	6	47	$51 MM	-	-	10%	150	1	-	10	18 MM	-		($15.83		$22.66		$26.14		$31.82
				$2 MM			50%								17.14		24.64		28.16		33.96
				$4 MM			75%								21.04		28.96		32.64		38.68
10	20	6	47	$2 MM	-	5	50%	-	1	-	0	18 MM	-	242		315		349		405	
											10			218		292		327		383	
											25			186		259		293		350	
11	20	6	47	$2 MM	-	-	50%	150	1	-	0	18 MM	-		9.72		13.46		15.23		18.13
											10				8.57		12.32		14.08		16.99
											25				6.85		10.60		12.37		15.27
12	20	6	47	$2 MM	-	5	50%	-	1	-	10	18 MM	-	218		292		327		383	
												X 1.5 ◆		348		421		456		512	
												X 0.6		116		189		223		280	
13	20	6	47	$2 MM	35 MM	0	50%	-	1	50	10	18 MM	23 MM	91		221		279		369	
						5								N.A		124		182		272	
						10								N.A		27		85		174	
14	20	6	47	$2 MM	35 MM	-	50%	150	1	50	10	18 MM	23 MM		N.A		3.44		6.39		11.25

* Alumina + Sulfur Plant

† Before credits, includes sulfur plant

‡ Units: $/ton (2000 lbs)

¥ Sludge credit, dry basis

◆ Non-material operating costs are varied by +50% and -40%

ton (10% DCF) and the sludge credit determined for a fixed alumina price of $150 per ton is $3.44 per ton (10% DCF). These values are to be compared with a base case value unattached alumina plant (Case 1), of $292 per ton for alumina and a corresponding credit for sludge, alumina price fixed, of $12.32 per ton (Case 2). A clear economic advantage rests with the combined cement-alumina complex. Case 13 also shows that for the combined plant, at a 12 percent DCF return rate, the alumina selling price escalates to no more than $182 per ton. This latter value compares favorably with the present market value of $160 per ton.

In all cases the utility supplying the sludge is being charged on a wet basis of zero to $10 per ton of wet sludge. Should a dry basis be employed, to accommodate variability in moisture percentage, the sludge credit would necessarily rise. However, the impact upon process economics may be slight. In the base case chosen for this report, a 50 percent solids - 50 percent water sludge is used. The sludge credit employed is $5 per ton on a wet basis. Should a dry basis be considered, the quantity of sludge upon which revenue is credited would be decreased by 50 percent. This, in turn, would decrease the total sludge credit by 50 percent if the $5 per ton price were maintained. It becomes necessary, therefore to increase the sludge credit per dry ton to compensate for loss of revenue. A $10 per dry ton credit is still competitive with alternate sludge disposal methods. If this value is chosen, the loss of revenue from switching to a dry basis is exactly compensated for and the total sludge revenue remains the same. Thus, the method upon which sludge credit is determined need not have a significant effect as illustrated in this base case. Sludge credits shown in Table 14 may be multiplied by a factor of two to obtain the required credit on a dry solids basis.

Variations in sludge water content do affect energy requirements and, hence, product selling price. The impact of differing water content is shown in Cases 8 and 9. Cost factors were selected to illustrate the economics of using this process as opposed to a throw away process for sludge. In Case 8, a constant annual sludge credit of $6,825,000 was assumed. This essentially sets the values of the 75 percent, 50 percent and 10 percent moisture sludges at $2.50, $5.00 and $9.00 per wet ton, respectfvely and correspondingly decreases the selling

price of alumina. In Case 9, the alumina price was fixed at $150/ton and the corresponding dry sludge credit was calculated.

Alumina prices as determined in the bulk of solo alumina plant cases are high relative to present market values. However, in certain cases, such as the $10 per ton sludge credit of Case 1 at 10 percent DCF, the calculated alumina selling price of $195 per ton is not infeasible with respect to possible rising bauxite prices.

The impact of coal cost is shown with respect to sludge credit in Case 3. As may be observed, increases in coal cost have a profound effect upon the sludge credit required to maintain a $150 per ton selling price for alumina. Considered from the extreme standpoint of a coal cost of $40 per ton and a fixed sludge credit of $5 per ton, an alumina price of $468 is required at 12 percent DCF. Alumina prices and related sludge credits are highly sensitive to coal costs in this energy intensive process. This fact may be compensated to a large extent by increases in sulfur credit. In the cases discussed above, a sulfur credit of $10 per ton was assumed. This value is conservative with respect to present market values in excess of $60 per ton. Cases 10 and 11 illustrate the relation between sulfur credit and alumina selling price-sludge credit. An increase from $10 per ton to $25 per ton sulfur credit will produce a 11 percent reduction in alumina selling price at 10 percent DCF.

The remaining raw material input, clay and Na_2CO_3, have been priced at $6 per ton and $47 per ton, respectively. These are conservative values. Clay may be mined at less cost than used in the base case, should a continguous mine be possible. The effect of reduced clay cost was determined in Cases 6 and 7. Sodium carbonate was set at the present market value F.O.B. This latter factor was not varied although some reduction in cost may be feasible.

REFERENCES

1. Rossoff, J. and R.C. Rossi, Disposal of By-Products from Non-Regenerable Flue Gas Desulfurization Systems, Vol. I. EPA-650/2-74-037, Aerospace Corp. El Segundo, Calif. 1974.

2. Cservenyak, F.J. Recovery of Alumina from Kaolin by the Lime-Soda Sinter Process. R. I. 4069, U.S. Dept. of the Interior - Bureau of Mines, College Park, Maryland, 1947. 59 pp.

3. Peters, F.A., P.W. Johnson, J.J. Henn, and D.C. Kirby. Methods for Producing Alumina from Clay. R. I. 6927, U.S. Dept. of the Interior - Bureau of Mines, College Park, Maryland, 1966. 38 pp.

4. TRW Systems Group, Inc. Proposal for the Development of a New Process for the Economic Utilization of the Solid Waste Effluent from Limestone Slurry Wet Scrubber Systems. Proposal No. 27359.000. 1974. Two volumes, 112 pp.

5. TRW Systems Group, Inc. Engineering and Cost Effectiveness Study of Fluoride Emissions Control, Vol. I. SN 16893.000. McLean, Virginia. 1972.

6. Peters, F.A. and P.W. Johnson. Revised and Updated Cost Estimates for Producing Alumina from Domestic Raw Materials. IC 8648. Bureau of Mines, College Park, Maryland, 1974. 51 pp.

7. McGlamery, G.G., et. al. Detailed Cost Estimates for Advanced Effluent Desulfurization Processes. EPA-600/2-75-006, Tennessee Valley Authority, Muscle Shoals, Alabama. 1975. 418 pp.

8. Bureau of Mines Staff. Mineral Facts and Figures, BuMines Bulletin 650, U.S. Government Printing Office, 1970. 1291 pp.

9. Lowenheim, F.A. and M.K. Moran. Industrial Chemicals, Fourth Edition. Wiley-Interscience. 1975. 904 pp.

APPENDIX A

GENERAL CONVERSION FACTORS

British			Metric	
	Multiply	By	To Obtain	
ac	acre	0.405	hectare	ha
bbl	barrels of oil	158.97	liters	l
Btu	British Thermal Unit	252	gram-calories	g-cal
°F	degrees Fahrenheit-32	0.5555	degrees Centigrade	°C
ft	feet	30.48	centimeters	cm
ft^2	square feet	0.0929	square meters	m^2
ft^3	cubic feet	0.02832	cubic meters	m^3
ft/min	feet per minute	0.508	centimeters per second	cm/sec
ft^3/min	cubic feet per minute	0.000472	cubic meters per second	m^3/sec
gal	gallons	3.785	liters	l
gpm	gallons per minute	0.06308	liters per second	l/sec
gr	grains (troy)	0.0648	grams	g
gr/ft^3	grains per cubic foot	2.288	grams per cubic meters	g/m^3
hp	horsepower	0.7457	kilowatts	kW
in	inches	2.54	centimeters	cm
lb	pounds	0.4536	kilograms	kg
lb/ft^3	pounds per cubic foot	16.02	kilograms per cubic meter	Kg/m^3
lb/hr	pounds per hour	0.126	grams per second	g/sec
mi	miles	1609.	meters	m
rpm	revolutions per minute	0.1047	radians per second	rad/sec
scfm	standard cubic feet per minute (32°F)	1.695	normal cubic meters per hour (0°C)	Nm^3/hr
ton	tons (short)*	0.90718	metric tons	t
ton,long	tons (long)*	1.016	metric tons	t
ton/hr	tons per hour	0.252	kilograms per second	kg/sec

* All tons, including tons of sulfur, are expressed in short tons in this report.

APPENDIX B

ECONOMICS MODELS - REVENUE REQUIREMENTS

Utility*: $R = N + .1198C + .01981W$

10% DCF†: $(.52[R-(N+D)]+D)\ 8.51356 = C - .14864W + .1875\ (C-W)$

12% DCF†: $(.52[R-(N+D)]+D)\ 7.46944 = C - .10367W + .225\ (C-W)$

15% DCF†: $(.52[R-(N+D)]+D)\ 6.25933 = C - .0611W + .281\ (C-W)$

where: R = Revenue required at indicated level of return

N = Net operating cost - $9,000,000

W = Working capital - $5,000,000

C = Total capital requirement (including working capital) - $52,000,000

D = Annual depreciation (5% of fixed capital) - $2,300,000

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* Utility financing assumes:

- debt/equity ratio = 75/25
- interest on debt = 9%
- return on equity = 15%
- income tax rate = 48%

† Discounted cash flow financing assumes:

- income tax rate = 48%
- DCF return rates as indicated above